SMALL CARBON CLUSTERS (C_n^0, C_n^+, C_n^-) FROM ACYCLIC AND CYCLIC PRECURSORS. NEUTRALIZATION-REIONIZATION MASS SPECTROMETRY AND THEORY

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Abstract: Ab initio calculations of isomeric carbon clusters C_n^0 and C_n^+, n = 2-4, yield structures and energies similar to previous reports, although five (not two) C_4^+ structures have local energy minima. Dissociative ionization of structurally varied precursors was used to prepare C_3 and C_4 ionic and neutral isomers; however, their mass spectra from collisionally activated dissociation (CAD) and neutralization-reionization (NR) under a wide variety of conditions are indistinguishable, indicating only one isomer or the same mixture of isomers. Likewise, CAD and NR spectra of C_4^+ and C_4^0 from $^{13}CH_2=CHCH=^{13}CH_2$ and C_3^+ and C_3^0 from $CH_2=^{13}CHCH_3$ show complete $^{13}C/^{12}C$ scrambling. CAD cross sections are consistent with $C_4^+ - C_6^+$ ions as mainly linear isomers and C_7^+ ions from cyclic precursors as mainly cyclic. Product abundances from the unimolecular dissociation of C_n^0, C_n^-, and C_n^+ allow the selection of thermodynamic data that should be of higher relative accuracy, such as 11.4 eV for the C_3 ionization energy from reported values of 10.0-13.0 eV.

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Carbon clusters were first studied spectroscopically using emission from interstellar clouds and other cosmic environments[1,2] and by mass spectrometry of carbon vapors.[3] As recently reviewed,[4,5] the chemistry of C_n molecules and ions in plasmas (carbon arcs, laser ablation)[2-6] and in the formation of polynuclear aromatics, diamond films,[7] and soot[2,8] has been the subject of extensive theoretical and experimental research. Of the latter, most studies have measured ionic species; in this study neutralization-reionization mass spectrometry (NRMS)[9] is used to investigate the isomers and energies of C_n^0, as well as C_n^+ and C_n^-, clusters for $n \leq 7$ by mass selection and neutralization of C_n^+ ions from linear, branched, and cyclic molecules.

Theoretical calculations have predicted for small C_n^0 species that odd-numbered clusters have lower electron affinities, closed shell ground states, and higher stabilities; for the cationic C_n^+ counterparts, a similar order of stability was indicated, whereas for C_n^- anions an opposite trend was found.[4,5,10-12] Although stable C_n^0 and C_n^+ ($n < 10$) structures were first predicted to be non-cyclic, more recent ab initio calculations show stability also for cyclic isomers,[4,5,11] with the two isomers close in energy for C_3^+,[11,13] C_4^0,[11,14] and C_4^+.[11]

In experimental studies, carbon vaporization, with and without postphotoionization, yields mass spectra with more abundant odd-numbered C_n^+ and even-numbered C_n^- clusters,[4,15-18] as predicted by theory. This is more indicative of the relative stabilities of C_n^+ and C_n^- than of C_n^0; as pointed out for C_n^+

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spectra by Bowers and co-workers,[16] the actual C_n^0 abundances measured by mass spectrometry depend significantly on ionization cross sections and C_n^+ stabilities. However, the high relative stability of C_3^0 is supported by its preferential loss from both C_n^+ [4,16-18] and C_n^-.[15] Mass-selected C_n^+ clusters undergoing metastable,[16] collisionally activated,[17,18a] and laser dissociation[4] also favor formation of C_n^+ species of odd-numbered n values.

Concerning isomeric characterization, evidence for open chain C_n^0 and C_n^+ has come from photoelectron,[19] infrared,[20] and microwave[2,21] spectroscopy, low energy C_n^+ dissociations,[16] and ion mobility values.[22] However, stable cyclic structures are indicated for C_{4-6}^0 neutrals and C_3^+ ions by coulomb explosion techniques,[23] and, from the same laboratory, for C_3^0 - C_7^0 neutrals by electron affinity measurements;[23c,24] these values are much lower than those reported earlier,[19] possibly because the cyclic isomers are present in <10% concentration,[23c] with this value dependent on laser/graphite interaction conditions.[24] Additionally, cyclic C_5^+ is indicated by infrared spectra using an argon matrix,[25] and a second, presumably cyclic, C_7^+ isomer by differences in bimolecular reactivity[18] and ion mobility.[22] All of these studies utilized high-temperature formation from elemental carbon of these clusters, whose formation entropy should favor linear isomers.[4]

In a novel approach that could avoid this entropic preference, Lifshitz and co-workers[17] utilized dissociative

electron ionization of cyclic perchlorinated molecules to generate C_n^+ with n = 3,5,6,7 and ≥ 10, but found no evidence that this method gave different isomeric structures than those generated by carbon vaporization. Here we have extended this approach in an attempt to prepare linear, branched, and cyclic C_n^+ ions; C_3^+ and C_4^+ have been studied the most extensively because their isomers are predicted to be stable and of closely similar energies.[4,11,13,14] Further, with NRMS[9,26] these mass-selected cations are then utilized to form the corresponding neutrals and anions. Product abundances from their competitive unimolecular dissociations are used to evaluate basic thermodynamic values proposed for C_n^0, C_n^+, and C_n^- (Table I),[4,5,27,28] for which major disagreements still exist. Additional theoretical calculations have been carried out to guide these experiments.

Experimental Section

Using a tandem double-focusing (EB-EB; E = electrostatic, B = magnetic sector) mass spectrometer described in detail elsewhere,[29] ions formed by 70-eV electrons are accelerated by 10 keV, mass selected by MS-I (EB), and undergo charge exchange collisions with a neutral target gas in a first collision cell (Cls-I) to form fast neutrals. The calcium neutralization experiments employed a special furnace for vaporization temperatures up to 800° C and special care to minimize Hg background (a reason that xenon was used as a high IE target

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instead of Hg).[29b] Residual ions are deflected electrostatically, and the fast neutrals are made to undergo collisional reionization in Cls-II to yield cations or anions; negative ions are also formed by charge reversal of the precursor cations with C_6H_6 in Cls-II. The resulting ions are mass separated in E-II and detected. For cross section values, the neutral beam flux is measured using a retractable channeltron multiplier at Cls-III before E-II. Following proposed conventions,[30] the designation $^+NR^+$, Na(85%T)/O_2(70%T) indicates a spectrum from cation neutralization with Na at 85% precursor transmittance, followed by residual ion deflection (slash) and reionization to cations with O_2 at 70% transmittance. Data acquisition, reduction, and computer control employed a PC-based computer system.[29c]

Specific ion precursors included: hexabromobenzene (c-C_6Br_6), hexachlorobenzene (c-C_6Cl_6), benzene (c-C_6H_6), hexachloro-cyclopentadiene (c-C_5Cl_6), 1,3-butadiene (n-C_4H_6), hexachloro-1,3-butadiene (n-C_4Cl_6), 1,4-dibromo-2-butyne (n-$C_4H_4Br_2$), 1-bromo-2-methylpropene (i-C_4H_7Br), 1,2-dibromo-2-methylpropane (i-$C_4H_8Br_2$), propene (n-C_3H_6), and cyclopropane (c-C_3H_6). $H_2^{13}C=CHCH=^{13}CH_2$ was synthesized adopting the procedure for the corresponding ^{14}C-isotopomer;[31] all other compounds, including $CH_2=^{13}CHCH_3$, were obtained commercially.

Theory. Standard ab initio molecular orbital calculations[32] were carried out using the GAUSSIAN 88 program[33] with geometry optimizations at the HF/6-311G(d) level using the Quadratic Convergence technique ($C_2^{+\cdot}$ and $C_3^{+\cdot}$ structures were also optimized

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at the UMP2/6-311(d) level). Harmonic vibrational frequencies were used both to characterize stationary points on the surface as minima (all frequencies real, representing equilibrium structures) or first-order saddle points (one imaginary frequency, representing transition structures), and (after scaling by 0.89) to calculate zero-point vibrational contributions to relative energies. Improved relative energies were obtained on the HF/6-311G(d) optimized geometries using Møller-Plesset perturbation theory (frozen core) terminated at second (MP2) and fourth (MP4) orders.

Results and Discussion

Theory. Our ab initio calculations (Table II) were designed to search for new stable isomers to guide the experimental investigation. A broader exploration of the energy surface was sought here by utilizing a larger basis set, 6-311G(d). Ab initio calculations for carbon clusters are notoriously difficult and often require multi-configuration methods in order to obtain correct electronic states and isomer relative energies.[4,5,10-14] However, this was impractical in these extensive calculations, so that some stable isomers and electronic states were not identified. As found previously,[13] triplet excitations in the MP4 treatment exaggerate the relative stabilities of some isomers (Table II), but yield heats of atomization that are in better agreement with the experimental data and with previous calculations that include triple excitation.

Repeated optimizations of the $C_2^{+\cdot}$ doublet found only the $^2\Sigma_u^+$

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state, while the multi-configuration calculations[33] find this as an excited state 275 kJ mol^{-1} above the first $\underline{a}^2\Pi_u$ doublet state. Similarly, our $C_2^{+\cdot}$ quartet state ($^4\Pi_g$), bond length 1.222 Å, corresponds to the first excited state, 116 kJ mol^{-1} above the previously identified $\underline{X}^4\Sigma_g^+$ ground state.[33] For the C_2^0 neutral found previously,[5,34] the global minimum is the $^1\Sigma_g^+$ state (bond length 1.24 Å), while the triplet corresponds to the $c^3\Sigma_u^+$ excited state; the triplet-singlet energy difference (101 kJ mol^{-1}) at MP4(SDQ) level is close to that published (113 kJ mol^{-1}),[33] but the lowest triplet state ($^3\Pi_u$) found previously[4,5] was not identified in our UHF geometry optimization. The cyclic $^2B_2$ C_3^+ isomer has been found by many recent multi-configuration calculations[14] to be 8-25 kJ mol^{-1} more stable than the linear $^2\Sigma_u^+$. We only find here the latter, a bent $^2B_2$ isomer, and a linear quartet state as local minima. Neutral C_3 calculations found the linear singlet ($^1\Sigma_g^+$),[5,35] bond length 1.275 Å, and triplet ($^3\Pi_u$) as ground and excited states, with an energy difference of 204 kJ mol^{-1}, MP4(SDTQ), close to the calculated (197 kJ mol^{-1})[36] and experimental (203 kJ mol^{-1})[37] values.

Two stable $C_4^{+\cdot}$ structures were identified previously by theory;[4,11] here an additional three were found as local energy minima (Table II and Figure 1). Of the species already identified,[4,11] we find the linear doublet $\mathbf{1}^+$ ($^2\Sigma_u^+$) to be the most stable $C_4^{+\cdot}$ species at the MP4(SDQ) level of theory, while the linear quartet $\mathbf{3}^+$ (^4B_g) of a slightly distorted zigzag geometry

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($D\infty_h \rightarrow C_{2h}$) is the most stable isomer at MP4(SDTQ). The cyclic ^{4}A" quartet 2^+ is another stable structure of a slightly distorted rhombus geometry ($D_{2h} \rightarrow C_s$). These distortions are likely artifacts of the UHF geometry optimization.[34] The calculated quartet states show significant spin contamination (Table II), suggesting the existence of other closely spaced high multiplicity states. Two other $C_4^{+\cdot}$ species, the cyclic trapezoid 4^+ ($^2A_2$ state) and the branched isomer 5^+ ($^2B_1$ state), although significantly less stable, also represent minima, motivating our experimental search for further stable isomers.

Our calculations of the C_4 neutral system (Table II) found no new isomers. Geometry optimizations led to the linear triplet, bond lengths 1.297 (end) and 1.274 Å, identified as the $^3\Pi_g$ state, but not to the corresponding ground $^3\Sigma_g^-$ state[11-14] lying 125-145 kJ mol^{-1} below. We also found rhombic (^1A_g) and linear ($^1\Sigma_g^+$) singlet isomers, 138 and 20 kJ mol^{-1} more stable than the triplet ($^3\Pi_g$), at the MP4(SDQ) level of theory, consistent with previous calculations.[14] However, the linear singlet energy is too low in the MP4(SDTQ) calculations (Table II).

Isomer Characterization from CAD and NR Spectra.
Collisionally activated dissociation, CAD [O_2(50%T)] of 10 keV C_2^+ - C_7^+ clusters gave the Figure 2 spectra; the previously reported CAD (air) spectra of 8 keV C_3^+, C_5^+, C_6^+, and C_7^+ ions are in agreement.[17,18a] However, our C_3^+ and C_4^+ spectra are independent (±10%) of the wide variety of precursor molecules used. Further,

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these spectra were not significantly changed by collisionally activating [He(50%T), first field-free region] the precursor ions to increase their average internal energy. The CAD spectra of C_6^+ from $\underline{c}-C_6Cl_6$ and $\underline{c}-C_6Br_6$, and of C_7^+ from toluene and cycloheptatriene also were closely similar.

NR mass spectra have been used successfully to differentiate a multiplicity of isomers for cations whose CAD spectra are closely similar, such as those of C_4H_8 and C_4H_4.[38] However, NRMS studies with the wide variety of C_n^+ precursors (Figures 3,4) found no isomeric differences outside experimental error. The C_n^+ charge exchange spectra [$^+NR^-$ C_6H_6(30%T), Figure 3] gave similar (±20%) data for C_3^+ and C_4^+, irrespective of the precursor used, and this was also true (±10%) for neutralization of C_n^+ with Xe, Na, or K followed by reionization [O_2(70%T), Figure 4].

All C_n^+ spectra from xenon neutralization (70%T; IE = 12.1 eV) are dominated by the reionized precursor peak, with fragment peak abundances closely similar to those in the corresponding CAD spectra; this is consistent with the formation of these fragments by dissociation of cations after reionization, not by neutral dissociation.[30] More excited neutrals can be formed by using a target of lower ionization energy (IE), thus removing less energy from the ion in the neutralization process.[9,26] Using Na or K (IE = 5.1 or 4.3 eV) greatly reduced the reionized precursor peak for C_4 - C_6 (Figure 4), consistent with a corresponding extent of neutral dissociation, but the fragment abundances were still independent (±10%) of the precursor molecule used for all C_n^+

ions studied.

The surviving precursor concentration from an intermediate extent of C_4^0 dissociation should yield a more sensitive test of isomeric identity than the abundances of the C_{1-3}^0 products, as dissociation could be preceded by isomerization of the C_4^0 precursor. Neutralization with calcium (IE = 6.1 eV) did provide partial C_4^0 dissociation (Table III), but $^+NR^+$ spectra from five different precursors still had closely similar abundances of reionized C_4^+ as well as C_{1-3}^+ fragment ions.

As a further test of the stability of the linear isomer of C_4^+ and C_4^0, $[1,4-^{13}C_2]-1,3$-butadiene was used as a precursor in an attempt to generate $^{13}C-^{12}C-^{12}C-^{13}C^+$. Its CAD $[O_2(70\%T)]$ and NR $[K(90\%T)/O_2(70\%T)]$ spectra showed intensity ratios for m/z 24:25:26 of 1.3:4.7:1 and 1.1:4.3:1, respectively, and ratios for m/z 37:38 of 0.99:1 and 1.00:1, respectively. For these peak abundances, single bond dissociation of $^{13}C^{12}C-^{12}C^{13}C$ without isomerization would yield 0:1:0 and 1:0, respectively; with complete scrambling, these ratios should be 1:4:1 and 1:1. Although isomerization is thus nearly complete, this does not necessarily indicate that the C_4^+ ion is not linear or that the linear C_4^+ ion is unstable, as isotopic scrambling could occur during formation of the C_4^+ ion by dissociative ionization of the butadiene. Similarly, the CAD $[He(70\%T)]$, NR $[K(90\%T)/O_2(70\%T)]$, NR $[K(90\%T)/He(70\%T)]$, and charge reversal $[C_6H_6(30\%T)]$ spectra of propene-2-^{13}C also showed similar scrambling. The intensity ratios of m/z 24:25 in these spectra were found to be 1:2.1,

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1:2.0, 1:2.2, and 1:2.1, respectively; complete scrambling should give 1:2. Again, the C_3^+ and/or C_3^0 structures are not necessarily non-linear or unstable. However, all of the above data are consistent with the formation of both C_3^+ and C_4^+ from the various precursors as single isomers or similar mixtures of isomers.

CAD and NR Efficiencies. As reported earlier,[4,16-18] the relative yields of C_n^+ in CAD spectra (Figure 2) are consistent with the expected higher stability of the odd-numbered cationic clusters. The relative efficiencies for CAD dissociation of C_n^+ (Table IV) also reflect this stability relationship, assuming increasing dissociation cross section with increasing size, as found for metastable ion (~10^{-5} s lifetime) dissociation.[16,17] Although mass discrimination[39] could affect the summed product cation abundances from CAD of C_n^+, the value for C_7^+ is substantially below those of C_4^+, C_5^+, and C_6^+. Metastable ion studies found a small[17] or significant[16] decrease in the cross section for C_7^+ versus C_6^+, but still greater than the value for C_5^+ (C_4^+ was not measured). For ion-molecule reactions of laser-generated C_7^+ ions, two-thirds were found to be unreactive with D_2, indicating that the majority of ions have the cyclic structure.[18] The relatively low degree of fragmentation for $C_7^+ \rightarrow C_{<7}^+$ (Table IV) indicates that C_7^+ is unusually stable and/or of smaller physical cross section for undergoing collision; either is consistent with a possibly higher fraction of cyclic isomers for C_7^+ prepared by dissociative ionization of cyclic precursors.

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As a corollary, this also implies that C_5^+ and C_6^+ are mainly the linear isomers. For the even-numbered, less stable C_4^+ and C_6+ clusters, the increase in $C_n^+ \rightarrow C_{<n}^+$ cross section values should be due primarily to increasing size, consistent also with a linear structure for C_4^+.

The $C_n^+ \rightarrow C_{\leq n}^0$ neutralization efficiency (Table IV) decreases quite regularly from C_1 (15.4%) to C_6 (4.9%); the increasing physical cross section apparently is more effective in producing scattering than electron transfer. The $C_n^0 \rightarrow C_{\leq n}^+$ reionization efficiency decreases even more dramatically from C_1 (5.2%) to C_6 (0.3%) despite decreasing IE values; neither the $C_n^+ \rightarrow C_n^0$ nor $C_n^0 \rightarrow C_n^+$ efficiencies reflect the odd/even nature of the cluster, consistent with the fact that odd clusters are more stable for both C_n^0 and C_n^+. In contrast, the efficiency for forming C_n^- from C_n, as well as the C_n^- ~~stability~~ shown by the $C_n^- \rightarrow C_{\leq n}^-$ values, favors the even-numbered clusters, as expected. Although the efficiency for $C_n^+ \rightarrow C_n^-$ drops substantially from C_2 (0.90%) to C_6 (0.14%), most of this appears to be due to the drop in neutralization efficiency, $C_n^+ \rightarrow C_n^0$; the negative effect of size is far less for $C_n^0 \rightarrow C_n^-$ than for the much higher energy $C_n^0 \rightarrow C_n^+$ process.

C_n^0 **Heats of Formation** (ΔH_f). The ΔH_f values of C_n^0 from experimental and theoretical studies (Table I) were checked for their ability to predict competitive product abundances from unimolecular dissociations (Figure 4) after neutralization. This assumes minimal entropy requirements; energy release measurements for C_n^+ metastable ion dissociations indicate negligible reverse

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activation energy.[16,17] Comparisons can only be qualitative because of serious mass discrimination against smaller product ions. For example (Figure 4) $[C_1^+]$, $\Delta H_f = 717$ kJ mol^{-1}, in the C_3^+ NR spectrum should even be higher than $[C_2^+]$; the smaller C_n^0 products have fewer vibrational degrees of freedom (none for C_1^0), so that a higher proportion of excess excitation energy could become translational energy, increasing loss of the smaller product. Offsetting this somewhat, these do have higher reionization efficiencies (Table IV), and their abundances are also increased by secondary product dissociation, as shown by K versus Na neutralization.

For C_4^0 NR data (Figure 4 and Table III), formation of C_1 + C_3 is somewhat favored over that of 2 C_2. Using $\Delta H_f(C_1^0) = 717$ kJ mol^{-1} as the reference value,[27] the pairs of $\Delta H_f(C_2^0, C_3^0)$ values (Table I) of (832, 837),[27] (815, 801),[11a] and (782, 773) predict that C_2^0 formation is 110, 115, and 74 kJ mol^{-1}, respectively, more endothermic than that of C_1^0 + C_3^0; even the 74 kJ mol^{-1} could be high. For C_5^0 dissociation, using $\Delta H_f(C_2^0, C_3^0)$ of 782 and 773 with $\Delta H_f(C_4^0) = 971$, 1022, and 1012 kJ mol^{-1} predicts endothermicities of 133, 184, and 174 kJ mol^{-1} favoring the formation of C_2^0 + C_3^0 over that of C_1^0 + C_4^0; again the Figure 4 data would appear to favor the lowest value (the C_4^0 reionization efficiency, Table IV, is half that of C_3^0). For C_6^0 dissociation using $\Delta H_f(C_2^0, C_3^0, C_4^0)$ of 782, 773, and 971 kJ mol^{-1} predicts an endothermicity of 207 kJ mol^{-1} favoring formation of 2 C_3^0 over

that of $C_2^0 + C_4^0$; this value appears more consistent with the Figure 4 data than those of 258 and 248 kJ mol^{-1} derived with $\Delta H_f(C_4^0) = 1022$ and 1012 kJ mol^{-1}. Using the $\Delta H_f(C_5^0)$ values of 979 and 1030 kJ mol^{-1} with these $\Delta H_f(C_2^0, C_4^0)$ values predicts endothermicities of 57 and 6 kJ mol^{-1} favoring formation of $C_1^0 + C_5^0$ over that of $C_2^0 + C_4^0$; to agree with the Figure 4 data and subsequent correlations, 979 kJ mol^{-1} has been chosen. These values, underlined in Table I, should be of higher relative accuracy than of absolute accuracy. These predict minimum energies of dissociation of C_2^0, 652; C_3^0, 726; C_4^0, 519; C_5^0, 576; and C_6^0, 343 kJ mol^{-1}, consistent with higher stability for the odd-n-value neutral clusters.

$\underline{C_n^0 \text{ Ionization Energies (IE)}}$. The agreement in reported IE values (Table I) is much poorer than even the accuracy presumed for our underlined ΔH_f values. For example, the 10.4 to 13.0 eV values reported for IE (C_3^0) are both substantially above, and substantially below, those of IE(C_2^0) and IE(C_4^0) (Table I). For this, comparison of the relative product yields in the NR and CAD spectra should be useful, as these should be affected mainly by the relative IE values, with mass discrimination at least qualitatively similar. Thus for the CAD spectrum of $C_3^+ \rightarrow C_1^0 + C_2^+$ vs. $C_2^0 + C_1^+$, the 0.8 eV predicted lower IE of C_1^0 should correspondingly favor C_1^+ formation versus that of C_2^+, consistent with the CAD (Figure 2) versus NR (Figure 4) spectra of C_3^+. Comparing the CAD and NR spectra of C_4^+, $[C_3^+]/[C_1^+]$ and $[C_3^0]/[C_1^0]$

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are similar, suggesting comparable $IE(C_3^0, C_1^0)$ values. The $[C_3^+]/[C_2^+]$ yield is several times that of $[C_3^0]/[C_2^0]$, again in agreement with the lower $IE(C_3^0)$ values found by theory, but not by other experiments (Table I); this is also borne out by the C_3/C_2 values in the CAD and NR spectra of C_5^+. The C_5^+ spectra also show that the $[C_4^+]/[C_3^+]$ yield is somewhat greater than that of $[C_4^0]/[C_3^0]$, indicating $IE(C_4^0) < IE(C_3^0)$; also consistent with this are the data of the C_6^+ CAD and NR spectra. For the C_6^+ spectra the $[C_5^+]/[C_4^+]$ yield is somewhat greater than that of $[C_5^0]/[C_4^0]$, although this is offset by the poorer reionization efficiency of C_5^0 vs. C_4^0 (Table IV). Thus the IE values of C_1^0 and C_3^0 should be comparable, with C_2^0 higher and C_4^0 and C_5^0 lower, consistent with the underlined values of Table I.

$\Delta H_f(C_n^+)$ Values. The heat of the formation values of the C_n^+ species, which represent the sum of the ΔH_f and IE values of the respective neutrals, can be used to predict the enthalpy differences in C_n^+ dissociation products of the CAD spectra (Figure 2). The best agreement with these data, again recognizing mass discrimination, was obtained using the underlined $\Delta H_f(C_n^+)$ values of Table I. From C_3^+, formation of C_2^+ is predicted to be <u>less</u> favored by 82 kJ mol^{-1}, but mass discrimination should greatly reduce $[C_1^+]$, which is still an abundant peak in the C_3^+ CAD spectrum. From C_4^+, C_1^+ formation is 13 kJ mol^{-1} favored over that of C_3^+, by far the most abundant peak, with C_2^+ less favored by 156 kJ mol^{-1}. From C_5^+,

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differential enthalpy values are C_4^+, 67; C_3^+, 0; C_2^+, 69, and C_1^+,

120 kJ mol^{-1}; from C_6^+, these values are C_5^+, 84; C_4^+, 141; C_3^+, 0;

C_2^+, 276; and C_1^+, 137 kJ mol^{-1}; and from C_7^+, these values are C_6^+,

89; C_5^+, 17; C_4^+, 0; C_3^+, 66; C_2^+, 152; and C^+, 229 kJ mol^{-1}. These

values are qualitatively (±30 kJ mol^{-1}) consistent with the

Figure 2 spectra. These predict minimum energies of dissociation

of C_2^+, 570; C_3^+, 713; C_4^+, 605; C_5^+, 642; C_6^+, 496; and C_7^+, ~777 kJ

mol^{-1}, consistent with higher stability for the odd-n-value

cation clusters.

NR Energy Deposition. The differences between these $\Delta H_f(C_n^+)$

values and the previous $\Delta H_f(C_n^0)$ values yield $IE(C_n^0)$ values

(underlined, Table I) that can be checked further against the

extent of C_n^0 precursor dissociation in the '$\mathcal{R}$ spectra. The

appropriate minimum internal energy E^*_{min} of C_n^0 after

neutralization is dependent on $IE(C_n^0)$ - $IE(target)$, with target

$IE(Mg,Na,K)$ = 6.1, 5.1, and 4.3 eV. As an example,[39]

neutralization of CH_4^+ (IE = 12.5 eV) with K should produce CH_4^0

with E^*_{min} = 12.5 - 4.3 = 8.2 eV. The product yields are CH_4^+, 0%;

CH_3^+, 53%; and CH_2^+, CH^+, and C^+; 47%. This results from

dissociation thresholds of 4.6 eV for CH_4^+ and 9.3 eV for CH_3^+,[27]

1.1 eV above E^*_{min}.

The neutralization of C_3^+ by Na (K) should produce C_3^0 with

E^*_{min} = 6.3 (7.1) eV; this causes 53% (75%) C_3^0 dissociation that

requires 7.5 eV, or 1.2 (0.4) eV above E^*_{min}. Neutralization of

C_4^+ by Mg (Na) should produce $E^*_{min}(C_4^0)$ = 4.6 (5.6) eV; this causes

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59% (94%) C_4^0 dissociation that requires 5.4 eV, or 0.8 eV above

(0.2 eV below) E^*_{min}. Neutralization of C_5^+ by Mg (Na) should

produce $E^*_{min}(C_5^0)$ = 4.6 (5.6) eV; this causes 28% (69%) C_5^0

dissociation that requires 5.8 eV, or 1.4 (0.4) eV above E^*_{min}.

Neutralization of C_6^+ by Mg (Na) should produce $E^*_{min}(C_6^0)$ = 3.7

(4.7) eV; this causes 75% (96%) dissociation that requires 3.6 eV

or 0.1 (1.1) eV below E^*_{min}. The agreement of these data with

each other, and with that of CH_4, is ~±0.3eV. An exce⌐ ᵢ is

C_2^0, which is only 32% dissociated. The excited electronic

states of the small C_2^0 molecule should have well separated

intersystem crossings, and thus some could have sufficiently long

lifetimes (>0.5 μs) to reach the reionization cell before

dissociation.

$\Delta H_f(C_n^-)$ **Values.** Such an evaluation for the negative ions

can be made using the charge exchange $^+NR^-$ spectra of Figure 3.

With the underlined values of Table I, all dissociations are

predicted to be highly endothermic (850 kJ mol^{-1} for C_2^-),

consistent with Figure 3. From C_3^- the formation of C_2^- is

predicted to be favored by 198 kJ mol^{-1}. From C_4^-, differential

enthalpy values are C_3^-, 58; C_2^-, 0; and C_1^-, 124 kJ mol^{-1}. From C_5^-,

, these values are C_4^-, 96; C_3^-; 132; C_2^-, 0; and C_1^-, 331 kJ mol^{-1}.

From C_6^-, these values are C_5^-, 68; C_4^-, 38; C_3^-, 0; C_2^-, 75; and C_1^-,

, 216 kJ mol^{-1}. Eyler has recently reported[28] electron affinities

for C_4^0, C_5^0, and C_6^0 of 1.3 - 1.5 eV, far lower than those derived

from the Table I values. Note that dissociation channels other

than those accompanied with C_3 neutral loss are also prominent, contrary to the photofragmentation results.[18] These $\Delta H_f(C_n^-)$ values predict minimum energies of dissociation of C_2^-, 850; C_3^-, 594; C_4^-, 630; C_5^-, 526; and C_6^-, 551 kJ mol^{-1}, consistent with higher stability for the even-n-value anion clusters.

Conclusions

Although multiple isomeric C_3^0 and C_4^0 species are predicted to be stable, those prepared from a wide variety of linear, branched, and cyclic (and isotopically labeled) precursors give NR spectra indicative of only one isomer, presumably the linear one. Consistent with results from gas-phase ion chromatography,[16] CAD cross sections indicate that C_5^+ and C_6^+ are also linear, but that C_7^+ is cyclic. Values of $\Delta H_f(C_n^0, C_n^+, C_n^-)$ and $IE(C_n^0)$ selected from previous experimental and theoretical studies, plus from calculations here, can be fit to reaction enthalpies consistent with these NR and CAD spectra, indicating values that should be of improved relative accuracy.

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Table I. Heats of Formation (298 K, kJ mol^{-1}) and Ionization Energies (eV); chosen values underlined.

Species		$\Delta H_f(C_n^0)$	IE	$\Delta H_f(C_n^+)$	$\Delta H_f(C_n^-)$[a]
C_1	expt[b]	<u>717</u>	11.3	<u>1803</u>	<u>595</u>
	theory[d]	717[c]	11.0	1778	
	theory[e]	717[c]	11.1	1788	
C_2	expt[b,f]	832	12.1	1998	505
	theory[d]	815[g]	12.1	1983	497
	theory[e,g]	<u>782</u>	<u>12.1</u>	<u>1950</u>[e]	<u>462</u>
C_3	expt[b]	837	12.1	2004	649
	expt[h]		13.0		
	theory	801[d]	<u>11.4</u>[d]	<u>1872</u>[g]	613
	theory[e]	<u>773</u>	10.4	1776	585
C_4	expt[b]	<u>971</u>	12.6[b,h]	2187	<u>614</u>
	expt[g]		<u>10.7</u>	<u>2004</u>	
	theory[d]	1022	10.5	2033	665
	theory[e]	1012	11.3	2102	655
C_5	expt	<u>979</u>[i]	11.5[i]	2024	<u>709</u>
	expt		12.3[h]	<u>2012</u>[g]	
	theory[d]	1030	<u>10.7</u>	2066	760
C_6	expt	$\geq$1180[k]	9.6[i]	$\geq$2106[i]	>784
	expt[h]		9.7		
	theory[d,l]	1203	9.8	<u>2149</u>	<u>807</u>
<u>c</u>-C_7	expt	$\geq$1146[k]		$\geq$1923[l]	$\geq$847
	theory[d]	<1263[m]		<2073[n]	<964
<u>n</u>-C_7	expt	>>1146[k,m]		>>2111[m,o]	>>847
	theory[d]	1263[m]		2227[p]	964

<u>Footnotes for Table I</u>.

[a]Using $\Delta H_f(C_n^0)$ plus vertical electron affinity (EA) values from ref. 19 except EA(C_1) from ref. 27; EA(C_3-C_6) from ref. 12 are lower by 28-40 kJ mol^{-1}. [b]From ref. 27. [c]Reference value used in the theoretical calculations. [d]Calculated from data (total electronic energy, fundamental frequencies, IE, etc.) of ref. 11a, with thermal corrections and heat of atomization (binding energy, 0 K) scaled by 1.1. [e]As in [d] from our calculations at the MP4 (STDQ) level; IE(C_2^0) from the total energy of the C_2^+ quartet state, corrected by the excitation energy $E(^4\Pi_g) - E(^4\Sigma_g^-) = 1.2$ eV from the MCSF-SCEP calculations, ref. 42; C_4 calculated for the rhombus structure. [f]Experimental value of 815 kJ mol^{-1} from Urdahl, R.S.; Bao, Y.; Jackson, W.M. <u>Chem. Phys. Lett.</u> 1991, <u>178</u>, 425-428. [g]From the present experimental data and the underlined IE values. [h]From ref. 28. [i]From ref. 18c. [j]Chase, M. W.; Davies, C. A.; Downery, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. <u>J. Phys. Chem. Ref. Data</u> 1985, <u>14</u>, Supplement 1: JANAF Thermochemical Tables, Third Edition. [k]Drowart, J.; Burns, R. P.; Demaria, G.; Inghram, M. G. <u>J. Chem. Phys.</u> 1959, <u>31</u>, 1131-1132. [l]Linear isomer (ref. 11a). [m]Assuming the cyclic isomer to be the more stable. [n]Using the theoretical IE value from ref. 18c. [o]Ref. 28; IE(linear) - IE(cyclic) = 1.6 eV from theory and 1.9 eV from experiment. [p]Using the IE value from Koopman's theorem.

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Table II . Calculated total energies of carbon cluster ions and neutrals.

Ion/ Neutral	$<S^2>$[b]	total energy[a]				
		SCF	MP2	MP4(SDQ)	MP4(SDTQ)	ZPVE[c]
C (^{1}P)	0	-37.598730	-37.669305	-37.694076	-37.694885	
C (^{3}P)	2.01	-37.689049	-37.745023	-37.763780	-37.764302	
C_2 ($^1\Sigma_g^+$)	0	-75.393686	-75.718201	-75.720480	-75.757361	11.4
C_2 ($^3\Sigma_u^+$)	2.01	-75.465389	-75.665165	-75.681075	-75.691228	14.3
C_3 ($^1\Sigma_g^+$)	0	-113.378370	-113.726307	-113.743722	-113.776683	23.2
C_3 ($^3\Pi_u$)	2.21	-113.283383	-113.645172	-113.659625	-113.697914	20.0
C_4 ($^1\Sigma_g^+$)	0	-151.166223	-151.758917	-151.628814	-151.859454	41.9
C_4 ($^3\Pi_g$)	2.28	-151.214780	-151.618959	-151.620997	-151.677634	42.4
C_4 (^1A_g)	0	-151.175999	-151.659151	-151.673560	-151.708357	35.3
C^+ (^{2}P)	0.76	-37.291796	-37.336540	-37.357692	-37.358019	
C^+ (^{4}P)	3.75	-37.158039	-37.167617	-37.170724	-37.170734	
C^{2+} ($^2\Sigma_u^+$)[d]	0.80	-74.922290	-75.161871	-75.170107	-75.188772	13.8
C_2^+ ($^4\Pi_g$)	3.75	-75.093854	-75.242087	-75.262514	-75.268205	13.2
C_3^+ ($^2B_2$)[e]	0.85	-112.938031	-113.301503	-113.311787	-113.343776	23.4
C_3^+ ($^2B_2$)[d]	0.85	-112.936514	-113.303785	-113.310393	-113.350904	
C_3^+ ($^2\Sigma_u^+$)[f]	0.78	-112.910338	-113.321953	-113.315460	-113.388621	22.5
C_3^+ ($^2\Sigma_u^+$)[d]	0.78	-112.908702	-113.323758	-113.317587	-113.394710	
C_3^+[g]	3.99	-112.977334	-113.231845	-113.255894	-113.272173	23.1
C_4^+ ($^2\Sigma_u^+$)	0.89	-150.828454	-151.237934	-151.280966	-151.307179	32.2
C_4^+ (^4B_g)	4.14	-150.776199	-151.237982	-151.264185	-151.308558	36.2
C_4^+ ($^2A_2$)	2.67	-150.814654	-151.181499	-151.219405	-151.240990	35.1
C_4^+ ($^4A''$)	3.86	-150.831167	-151.246165	-151.265529	-151.293238	36.1
C_4^+ ($^2B_1$)	1.37	-150.731486	-151.100270	-151.150165	-151.173292	27.3

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Footnotes for Table II .

Table III. $^+NR^+$ Spectra of $C_4^{+\cdot}$, Ca($\sim$85%T)^a/O$_2$(70%T).

Precursor	m/z	12	24	36	48
n-C$_4$H$_6$		5	16	56	23
n-C$_4$Cl$_6$		6	16	60	19
c-C$_5$Cl$_6$		6	14	60	21
c-C$_6$H$_6$		5	19	56	19
c-C$_6$Cl$_6$		7	17	58	18

^{a}Transmittance from 690°C Ca vaporization.

Table IV. Cross Sections for CAD and NR Spectra.

Cluster	C_n^+ [a] $\rightarrow C_{<n}^+$	C_n^+ [b] $\rightarrow C_{\leq n}^0$	C_n^+ [c] $\rightarrow C_{\leq n}^-$	C_n^0 [d] $\rightarrow C_{\leq n}^+$	C_n^- [e] $\rightarrow C_{<n}^-$
C_1	–	15.4	0.40	5.2	–
C_2	0.28	12.6	0.90	2.1	<1
C_3	0.42	9.8	0.23	1.8	18
C_4	1.8	7.7	0.24	0.90	25
C_5	1.8	6.3	0.09	0.60	37
C_6	2.8	4.9	0.14	0.30	20
C_7	0.80	–	–	–	–

[a] C_n^+ CAD, O_2(50%T), efficiency: total C_n^+ product ion abundance, in % of unattenuated precursor ion abundance (±20% relative). [b] C_n^+ neutralization, Xe(70%T), efficiency: total $C_{\leq n}^0$ flux, % of unattenuated precursor ion abundance (±10% relative). [c] C_n^+ charge reversal, C_6H_6(30%T), efficiency: total $C_{\leq n}^-$ abundances, % of unattenuated precursor abundance (±20% relative). [d] C_n^0 [from Xe(70%T) neutralization of C_n^+] reionization, O_2(70%T), efficiency: total $C_{\leq n}^+$ abundances, % of total $C_{\leq n}^0$ flux (±20% relative). [e] $C_{\leq n}^-$ dissociation efficiency in charge reversal spectra, C_6H_6(30%T): total $C_{<n}^-$ product ion abundance, % of survival C_n^-.

Figure Legends

Figure 1   Calculated geometries of C_4^+: $\underline{1}^+$, $^2\Sigma_u^+(D_{\infty h})$; $\underline{2}^+$, $^4A''(D_{2h} \rightarrow C_s)$; $\underline{3}^+$, $^4B_g(D_{\infty h} \rightarrow C_{2h})$; $\underline{4}^+$, $^2A_2(C_{2v})$; $\underline{5}^+$, $^2B_1(C_{2v})$.   Bond lengths are in Angstroms.

Figure 2   CAD spectra, $O_2(50\%T)$, identical ($\pm10\%$) for the same ion from the listed precursors: (A) C_2^+ from $\underline{n}-C_3H_6$, $\underline{n}-C_4Cl_6$;   (B) C_3^+ from $\underline{n}-C_3H_6$, $\underline{n}-C_4Cl_6$, $\underline{c}-C_3H_6$, $\underline{c}-C_5Cl_6$;   (C) $C_4^{+\cdot}$ from $\underline{n}-C_4H_6$, $\underline{n}-C_4H_4Br_2$, $\underline{n}-C_4Cl_6$, $\underline{i}-C_4H_8$, $\underline{i}-C_4H_7Br$, $\underline{i}-C_4H_8Br_2$, $\underline{c}-C_5Cl_6$, $\underline{c}-C_6H_6$, and $\underline{c}-C_6Cl_6$;   (D) C_5^+ from $\underline{c}-C_5Cl_6$;   (E) C_6^+ from $\underline{c}-C_6Cl_6$ and $\underline{c}-C_6Br_6$; and (F) C_7^+ from toluene and cycloheptatriene.

Figure 3   Charge reversal $^+NR^-$ spectra, $C_6H_6(30\%T)$, identical ($\pm20\%$) for the same ion from the listed precursors: (A-F) C_1^+-C_6^+, respectively, as in Figure 2, except C_4^+ is from $\underline{n}-C_4Cl_6$, $i-C_4H_7Br$, and $\underline{c}-C_5Cl_6$.   Higher trace is amplified tenfold.

Figure 4 $^+NR^+$ spectra, $Y/O_2(70\%T)$, identical ($\pm10\%$) for the same ion from the listed precursors: (A) C_1^+, (B,G,L) C_2^+, (C,H,M) C_3^+, (D,J,N) C_4^+, (E,J,O) C_5^+, (F,K,P) C_6^+, with (A-F) Y = Xe(70%T), (G-K) Y = Na(85%T), (L-P) Y = K(90%T). Precursors as in Figure 2, except C_3^+ is from $\underline{n}-C_3H_6$ and $\underline{n}-C_4Cl_6$ and also from $\underline{c}-C_3H_6$ and $\underline{c}-C_5Cl_6$ with K neutralization; C_4^+ is from $\underline{n}-C_4Cl_6$, $\underline{i}-C_4H_7Br$, and $\underline{c}-C_5Cl_6$ and also from $\underline{c}-C_6Cl_6$ with Na and K neutralization. Numeric values for precursors are the % of the value with no collisions (value for Mg neutralization in parenthesis.) Product values are relative peak areas, corrected for dissociation after reionization indicated in the Xe spectra, averaged for the multiple measurements.

Figure 1

C —1.363— C —1.230— C — C

1⁺

C —1.291— C —1.274— C — C

3⁺

C 1.373 C 1.524 67.5° C C

2⁺

C 1.435 C 92.7° 1.352 1.561 C C

4⁺

126.3° C 1.589 C 1.352 C C

5⁺

Figure 2

Figure 3

Figure 4